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Electrochemical Cell For Obtaining Oxygen From Carbon Dioxide Atmospheres

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Electrochemical Cell For Obtaining Oxygen From Carbon Dioxide Atmospheres

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Table of Contents

| Introduction | 1 |
|--|----|
| Tape Casting Experimental Thermal Treatment | 6 |
| Ceramic-to-Ceramic Seals | 11 |
| Electrodes Electrode Selection Electrode Application | 13 |
| Cell Design | 14 |
| Summary | 16 |
| Appendix A - Diffusion | |
| Appendix B - Tape Casting | |
| Appendix C - Cell Design | |
| References | |

Introduction

For manned missions to Mars to become a reality, an efficient and reliable means of extracting oxygen from the carbon dioxide-rich atmosphere will be required. Otherwise the high cost of transporting the oxygen necessary to support human life would severely restrict the mission to Mars.

Recently, the use of electrochemical devices has been examined as a means of obtaining oxygen from the Martian atmosphere. Electrochemical systems rely upon the transport of oxygen ions through a solid oxide electrolyte. This phenomenon was first discovered in 1899 by Walter Nernst. He observed that stabilized zirconia (ZrO₂) will conduct oxygen ions when an electric potential is applied across metallic electrodes applied to the ceramic membrane. Diatomic oxygen molecules (O₂) are dissociated at the positive electrode/electrolyte interface. The oxygen ions (O⁻²) enter the ceramic body due to the ion density gradient which is produced by the electrical potential across the electrolytic membrane. Once the oxygen ions have diffused through the membrane, they reform diatomic oxygen molecules at the anode.[1,2]

A variation of this process can be utilized to obtain oxygen from carbon dioxide. Oxygen is liberated from carbon dioxide by a thermal decomposition reaction that takes place at 1000°C. The decomposition of carbon dioxide into carbon monoxide and oxygen proceeds as follows:

$$2CO_2 \longrightarrow 2CO + O_2$$

The oxygen obtained from the thermal decomposition of carbon dioxide can

then be obtained via an electrolytic process.

Research has shown that the material best suited for this application is eight mole percent yttria (Y_2O_3) stabilized zirconia. The presence of yttria in the atomic structure of zirconia induces oxygen vacancies by the reaction:

$$Y_2O_3$$
 $ZrO_2 > 2Y_{Zr}^{-1} + O_0 + [V_0^{+2}]$

The reaction indicates that as yttrium atoms take the place of zirconium atoms in the crystal lattice, oxygen vacancies with a valence of +2 result. These vacancies act as charge carriers for oxygen ions in electrolytic systems.[2,3]

Yttria stabilized zirconia exhibits superior electric and ionic conductivities than any of the other stabilized zirconia compounds. Furthermore, this compound also possesses a high mechanical strength at the operating temperature of the device (1000°C). In addition to the attractive mechanical properties of this material, yttria stabilized zirconia can also withstand higher voltage applications than the other stabilized zirconia compounds.[2]

To utilize these properties, stabilized zirconia membranes must be produced in a manner that will result in the cell possessing a high surface-to-volume ratio. This value should be as high as possible to obtain as large a quantity of oxygen as possible in as small a space as possible.

In addition to the basic requirement that the electrolyte possess a large active surface area, the cell itself must also meet two important criteria. First, each component of the cell must possess similar thermal expansion coefficients. Otherwise, the cell's structural integrity will decline upon

exposure to thermal cycling. Secondly, each seal present in the device must be gas-tight and mechanically sound to ensure that the critical oxygen supply is not contaminated by the carbon dioxide atmosphere.

In addition to these overall design constraints, the electrolyte itself should be as thin as possible to allow for oxygen to diffuse through the membrane as rapidly as possible. Furthermore, the electrolyte should also be dense. The density of membranes used in oxygen transport systems has been found to influence the oxygen diffusivity and electrical conductivity of the system.[4] Thus, to develop an electrochemical device for obtaining large quantities of oxygen from Martian atmosphere, thin, pore free membranes must be produced.

Tape Casting

Tape casting is a ceramic forming technique used in the production of thin, high surface area substrates, especially for the electronics industry.[5,6] For product thicknesses in the 1 to 50 mil range, this technique is more suitable than other traditional forming methods such as dry pressing or extrusion. The process begins with the suspension of ceramic powder in a volatile solvent; the resulting slip is then spread upon a moving surface by a doctor-blade (a troweling device) and allowed to dry. Evaporation of the solvent vehicle leaves a thin substrate which can be cut or punched into desired shapes prior to heat treatment. Processes of this genre have been used extensively in the manufacture of dielectrics, piezoelectrics, and various substrates for electronic use.

In general, large scale continuous tape casting processes consist of a doctor-blade/slip basin device, a casting table, a surface to which the coating is applied, and a motor that draws the surface beneath the doctor-blade. First, the doctor-blade is simply a container that allows the slip to escape in the direction of surface motion by means of a small blade-edged opening at the base of the front wall. Adjustment of the height of this opening, and thus the tape thickness, is possible by precision set screws mounted on the blade

frame, and the blade itself is often beveled to reduce turbulence in the outflowing slip. Beneath the doctor-blade moves a surface which is to be coated. The material from which the surface is fabricated must be flexible (to permit rolling) and compatible (that is, inert) with respect to the slip components. Various plastics are candidates if the flexibility criterion alone is used; however, the solvent system employed must be considered. Due to the high drying rates needed in order to completely remove the solvent while on the casting table, highly volatile organic solvents are commonplace. The inertness of a plastic (or other surface material) versus the chosen solvent system must be evaluated prior to casting. Immediately after casting, the tape enters a drying zone where the solvent and any other volatile forming aids are removed. This zone is simply a section of the casting table that allows evaporation and some tape casting operations include blowers or dryer units for this purpose. Finally, a motor located at the front (finished product) end of the casting table draws the surface beneath the doctor-blade while rolling the produced tape (and plastic surface) upon a spindle. Tapes are later peeled away from the plastic carrier and prepared for the cutting and firing processes. Ideally, a variable speed motor should be used to allow for casting or drying rate alterations.

The tape casting apparatus used for the production of the zirconia oxygen cell at Clemson University follows the principle of industrial design with some modifications. The continuous feed of

the carrier surface (and, therefore, large rolls and winding devices) is eliminated in favor of a stationary glass plate that is covered with a thin sheet of the carrier. The moving part then becomes the doctor-blade itself, which is pulled by a variable speed chain drive located at the rear of the casting table. Drying of the slip takes place on the glass plate, which can be removed from the casting table almost immediately after casting, permitting several batches of slip to be cast in sequence. With this reduced design, tapes of high quality and useful dimensions (12.5 by 25 cm) can be produced rapidly and with only a fraction of the space required by an industrial tape casting apparatus.

EXPERIMENTAL

The development of a castable slip formulation requires the selection of compatible solvent, binder, and plasticizer systems that produce the desired tape properties such as green strength, flexibility, and suitable volatilization. Since little published data exists regarding the tape casting of zirconia, application of an established batch formulation for alumina tapes was used as a starting point. A common recipe for alumina tape casting includes trichloroethylene and ethyl alcohol (solvents), menhaden fish oil (deflocculant), polyvinyl butyral (binder), and Santicizer (plasticizer). Due to slight property differences between ZrO₂ and

Al₂O₃, the alumina slip recipe was altered to provide optimum strength and viscosity (see TABLE 1).

TABLE 1

| Material | Function | Parts by weight | |
|----------------------|-------------------|-----------------|--|
| ZrO2 powder (0.8 μm) | substrate materia | l 100.0 | |
| Menhaden fish oil | deflocculant | 2.3 | |
| trichloroethylene | solvent | 39.0 | |
| ethyl alcohol | solvent | 15.0 | |
| polyvinyl butyral * | binder | 5.0 | |
| Santicizer * | plasticizer | 7.9 | |

^{*} products of Monsanto, Inc.

Batch mixing occurred in two steps. First, the stabilized zirconia powder, solvents, and deflocculant were combined and ball-milled with partially-stabilized zirconia media for approximately 24 hours. The binder and plasticizer were then added, causing a sharp viscosity increase, and the batch was milled an additional 24 hours to insure uniform binder/plasticizer concentration. If the binder and plasticizer were unevenly distributed, areas of different strength and flexibility, which caused cracking during drying, resulted in the as-poured tapes. Once the recipe for a suitable slip

had been determined, a carrier surface was selected on the basis of compatibility with the slip's organic constituents. Several surfaces, such as cellulose acetate (Mylar), polyolefin, Teflon, glass, aluminum foil, and polyethylene, were evaluated. Chemical incompatibility, as in he case of polyvinyl butyral attack of cellulose acetate, and frictional resistance cracking during solvent removal prevented the use of the majority of these surfaces. Only polyethylene with a Menhaden fish oil lubricant showed any promise, and then only for limited tape sizes. Tapes of approximately 0.25 mm thickness were produced in this manner.

At that point, a different binder/solvent system was sought to eliminate the solvent removal difficulties. A batch recipe currently in use at Clemson University in the tape casting of electronic substrates includes trichloroethylene (solvent) and Binder 73171, a product of Metoramic Sciences, Inc. (see TABLE 2).

TABLE 2

| Material | Function | Weight percent |
|----------------------|-------------------|----------------|
| ZrO2 powder (0.8 μm) | substrate materia | 33.3 |
| Binder 73171 | binder | 33.3 |
| trichloroethylene | solvent | 33.3 |

In this recipe, the binder and solvent are mixed in equal parts by weight to form a thin liquid. The stabilized zirconia powder is added and ball-milled until there are no agglomerates present to produce the casting slip. This slip allowed adequate solvent removal while proving chemically inert with respect to the polyethylene casting surface; tapes of 0.1 to 0.5 mm thickness were produced by this procedure.

THERMAL TREATMENT

Final mechanical and electrical properties of the tapes are achieved during the thermal treatment (or firing) process. It is desired for the tapes to reach nearly theoretical density during treatment to provide the maximum strength and most efficient oxygen transport. Thus, the maximum temperature of firing was that sufficient to provide acceptable density and resulting properties for the tapes. Rate of treatments must also be considered in order to prevent damage, in the form of warping or cracking, to the final product. These aspects of firing, as well as furnace description, will be discussed here.

Zirconia sinters (or, densifies in the solid state) at approximately 1600°C. Therefore, maximum densities can be obtained by treating thin tapes for a short time above 1500°C. The critical portion of the firing schedule, however, is the selection of firing rate, especially in the lower temperature region. Here the organic

constituents of the batch, which provide green strength, are volatilized. Reduced initial heating rates reduce the chance of cracking during binder loss and short soak times at chosen temperatures within the treatment schedule allow for the completion of organic removal or chemical reaction. With these factors considered, the firing schedule implemented for the fuel cell tapes is as follows:

- 1. heat at 1.25°C/min to 75°C and hold for one hour,
- 2. heat at 1.25°C/min to 125°C and hold for one hour,
- 3. heat at 1.25°C/min to 250°C and hold for one hour,
- 4. heat at 2.50°C/min to 500°C and hold for one hour,
- 5. heat at 2.50°C/min to 800°C and hold for one hour,
- 6. heat at 5.00°C/min to 1200°C and hold for one hour,
- 7. heat at 5.00°C/min to 1550°C and hold for two hours,
- 8. cool to room temperature (~25°C) within furnace.

The furnace used in the production of all fuel cell tapes at Clemson University is a high-temperature laboratory furnace manufactured by Lindberg, a division of General Signal, Inc. This furnace is equipped with molybdenum disilicide electrical resistance heating elements and capable of continuous service at 1600°C. A set point controller with maximum power limit and proportional bandwidth selection provided adequate control of the firing process.

Ceramic-to-Ceramic Seals

To assemble the electrochemical device, the stabilized zirconia tapes must be bonded in order to form a rigid oxygen cell. Strength at the high temperatures required for the electrolysis/diffusion process and the deleterious effect of impurities are prime factors in the choice of a bonding agent. During cell operation, the bond must assume and retain the cubic structure of stabilized zirconia as well as closely match the thermal expansion of the tapes to prevent cracking.

A material that fits these criteria is zirconium phosphate.

Phosphates have traditionally been used in refractory patching applications because of the high strength of phosphate bonds at elevated temperatures. Ease of application, low curing temperatures, and high strength within the cell operating temperature range are advantages provided by this material.

Zirconium phosphate is formed by the addition of 8% Y₂O₃-stabilized ZrO₂ (fully stabilized zirconia) to phosphoric acid according to the following equation:

$$ZrO_2 + 4H_3PO_4 \longrightarrow Zr(H_2PO_4)_4 + 2H_2O.$$

This reaction results in a white, amorphous gel and chemically free water. Once the water has been thermally removed, the gel can be applied to the tape surfaces by dipping or brushing. The material is cured by heating in air to 400°C for 1 hour, resulting in a high-

strength bond.

Since the electrolysis process is dependent upon the diffusion characteristics of fully stabilized (cubic) zirconia, any phases exhibiting a non-cubic crystal structure reduce cell efficiency. A primary concern is that the zirconium phosphate would assume a different crystal structure and become a barrier to oxygen vacancy transport. However, X-ray diffraction studies have shown that the bond material exists in a cubic form after cycling between room temperature and cell operation temperature (1000°C).

Zirconium phosphate then appears to be an ideal bonding agent for the electrolysis cell. The high strength and refractoriness alone warrant its consideration; but the ability to maintain the desired crystal structure throughout cell operation permits its use.

Electrodes

Electrode Selection

For the electrochemical device to operate efficiently, a suitable electrode material must be selected and applied to the surface of the electrolyte. Many noble metals have been examined as candidate materials for employment in electrochemical devices. However, only platinum possesses the high electrical conductivity at elevated temperatures required for this application. Additionally, platinum has a similar thermal expansion to zirconia, thus reducing the potential adverse effects associated with thermal cycling.[7]

Upon long term exposure to carbon-based atmospheres, the electrical conductivity of platinum has been found to decline. Due to this fact, research is currently being done with regard to the production of solid state ceramic electrodes. The development of these electrodes would provide an inexpensive alternative to platinum, and their use in systems of this type would drastically reduce the cost.

Electrode Application

To apply the platinum to the electrolyte, a process similar to silk screening [8] was adopted. This process involved the application of a platinum ink onto the zirconia membrane. The platinum was applied in a grid that optimized the amount of surface area electrolyzed while minimized the actual area of the electrolyte concealed by the electrode.

Cell Design

An electrochemical device for obtaining large quantities of oxygen must possess a high surface-to-volume ratio. This will allow the cell to obtain large quantities of oxygen while occupying a limited space. The utilization of thin ceramic membranes as the electrolyte in these devices will provide the necessary high surface-to-volume ratio to develop an efficient device.

In addition to possessing a high surface-to-volume ratio, electrochemical cells must also constructed from components with similar thermal expansions. Otherwise, the thermal cycling encountered in the operation of the device will result in the degredation of the cell's structural integrity over time.

Thicker membranes (0.5 mm) were used to construct the body of the cell. The use of these membranes provides the cell with a greater structural stability than it would otherwise have if constructed from thinner membranes. The zirconia membranes that serve as the electrolyte is thinner (0.1 mm) to allow for a more rapid obtainment of oxygen from the carbon dioxide environment. The electrolytes are arranged in a series of slanted, connected membranes. (See appendix C) The membranes are oriented in this manner to increase the surface-to-volume ratio of the cell.

To provide the cell with the voltage supply necessary to catalyze the reaction, platinum wires were connected across each ridge in the electrolytic surface. To ensure that the electrical contact was sufficient,

the ridges were coated with an extra layer of platinum ink.

The proposed cell design is unique in that it does not require a complex manifold system for separating the gases in the system. The bottom of the system is open to allow for the free flow of carbon dioxide into the cell. By operating the cell at 1000°C, the carbon dioxide will decompose the carbon dioxide into carbon monoxide and oxygen. The oxygen, when in contact with the electrolytic surface will be, will be split into negatively charged ions and passed through the vacancies present in the zirconia structure. The oxygen will then be collected and stored for use in the life support system or as fuel.

Summary

To support human life on the Martian surface, an electrochemical device will be required to obtain oxygen from the carbon dioxide rich atmosphere. The electrolyte employed in such a device must be constructed from extremely thin, dense membranes to efficiently acquire the oxygen necessary to support life.

A forming process used industrially in the production of multilayer capacitors and electronic substrates was adapted to form the thin membranes required. The process, known as tape casting, involves the suspension of extremely fine particles (<1µm in diameter) in an organic suspension consisting of solvents and binders. The suspension is passed under a blade, resulting in the production of ceramic membranes between 0.1 and 0.5 mm thick.

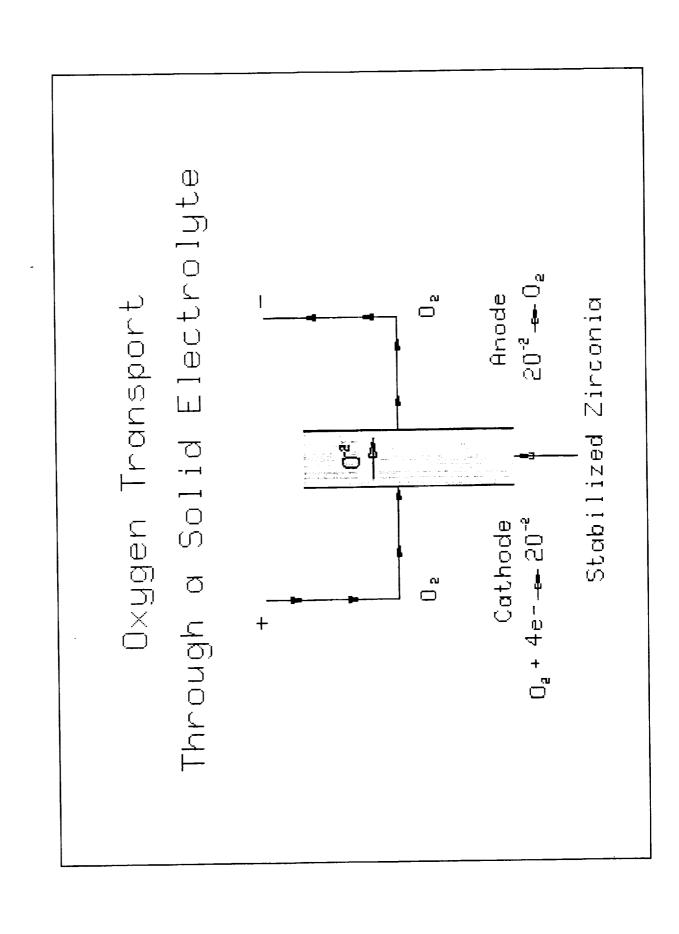
Once fired, the stabilized zirconia membranes were assembled into the cell design by employing a zirconium phosphate solution as the sealing agent. The resulting ceramic-to-ceramic seals were found to be structurally sound and gas-tight. Furthermore, by using a zirconia-based solution to assemble the cell, the problem of a thermal expansion mismatch was alleviated.

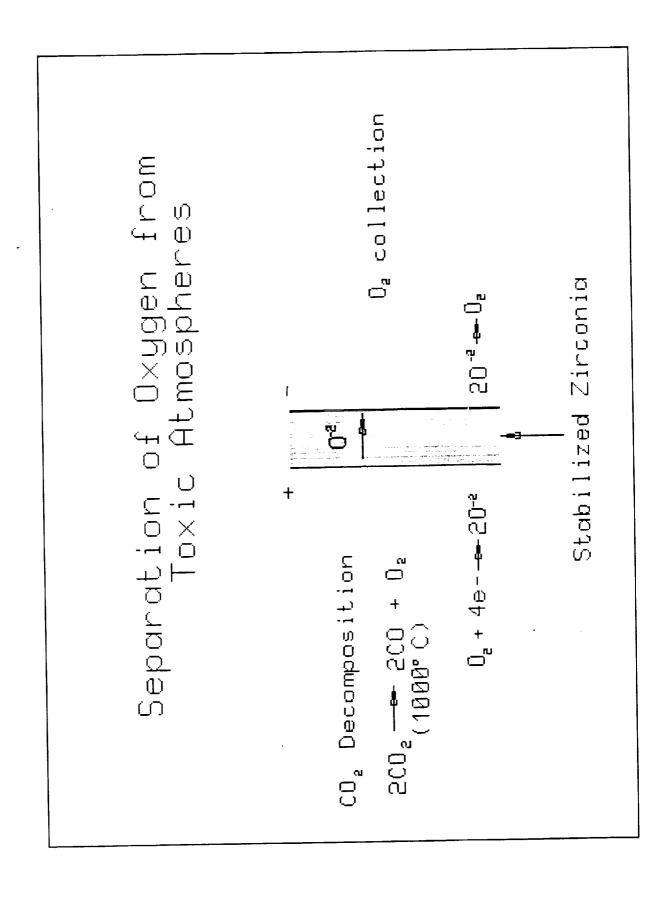
By adopting an industrial forming process to produce thin membranes, an electrochemical cell for obtaining oxygen from carbon dioxide was produced. The proposed cell design is unique in that it does not require a

complicated manifold system for separating the various gases present in this process, nor does it require a series of complex electrical connections. Thus, the device can reliably obtain the vital oxygen supply from the toxic carbon dioxide atmosphere.

Appendix A

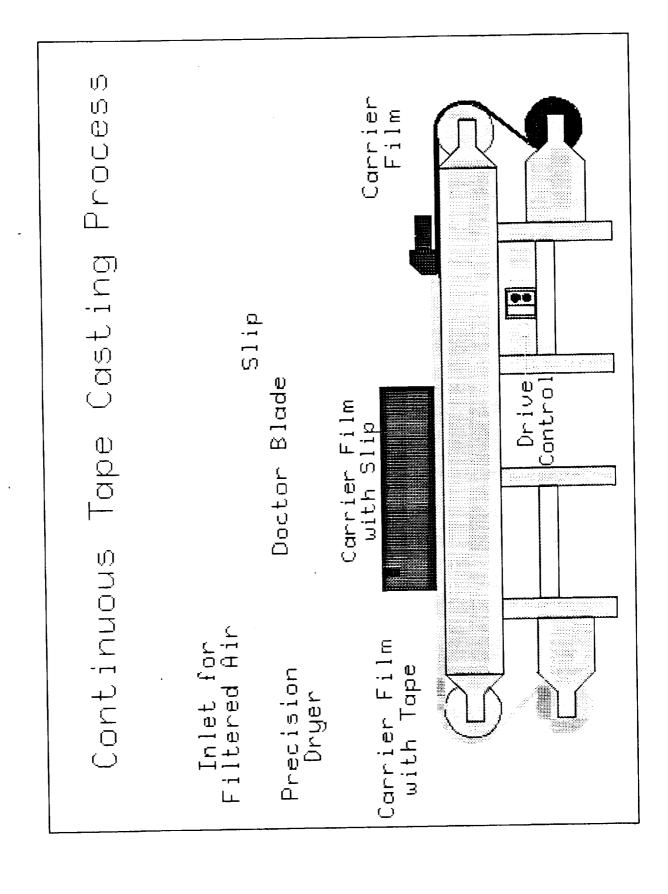
Diffusion

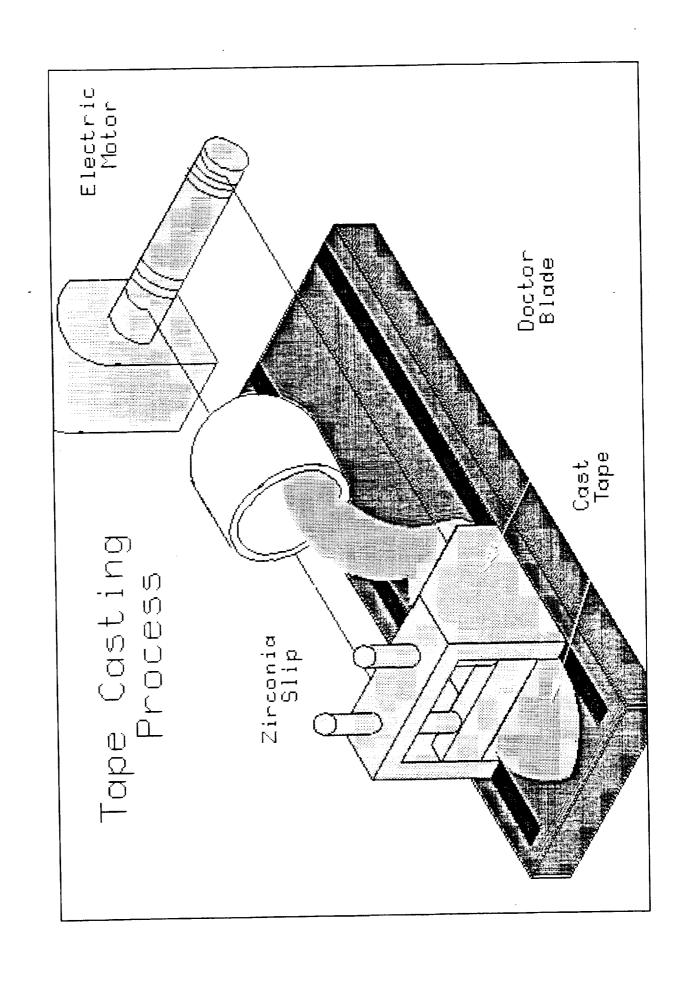


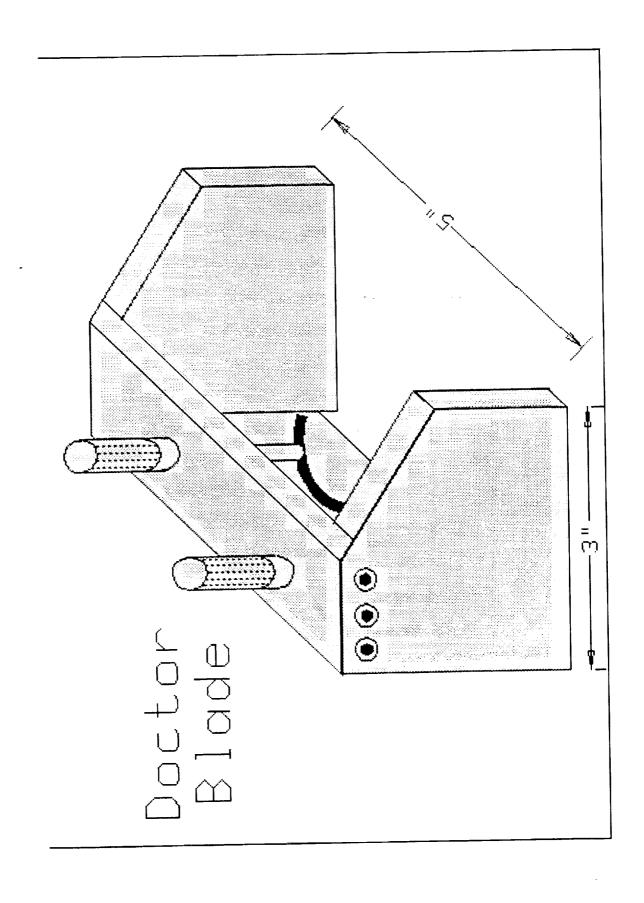


Appendix B

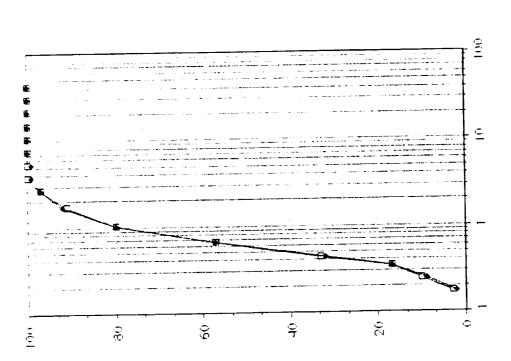
Tape Casting





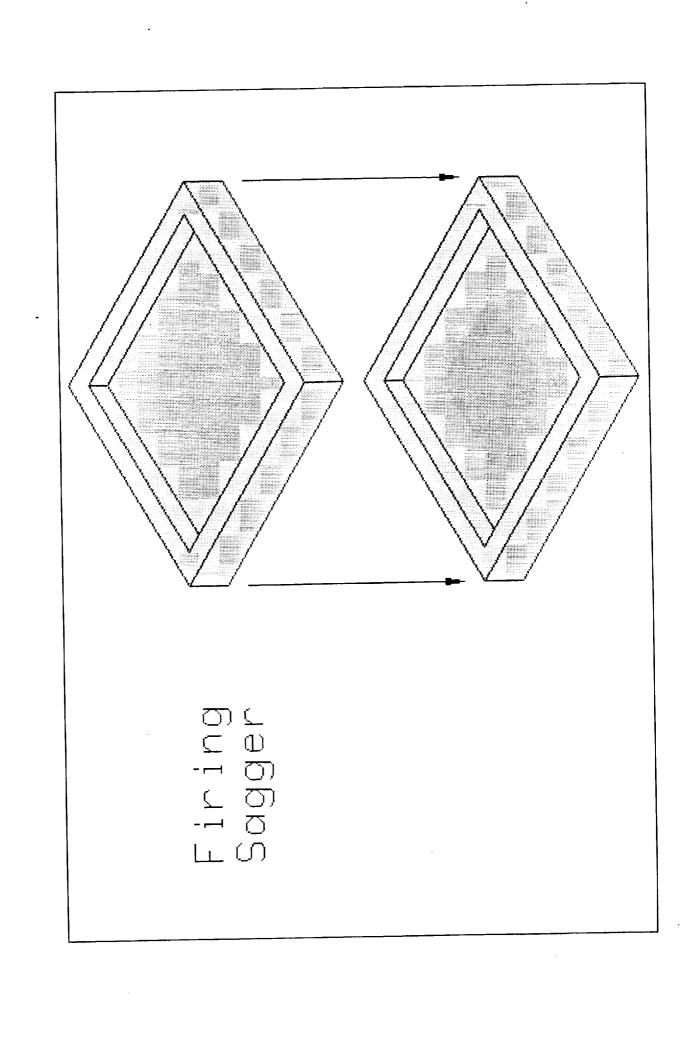


Particle Size Distribution of Zirconia Powder



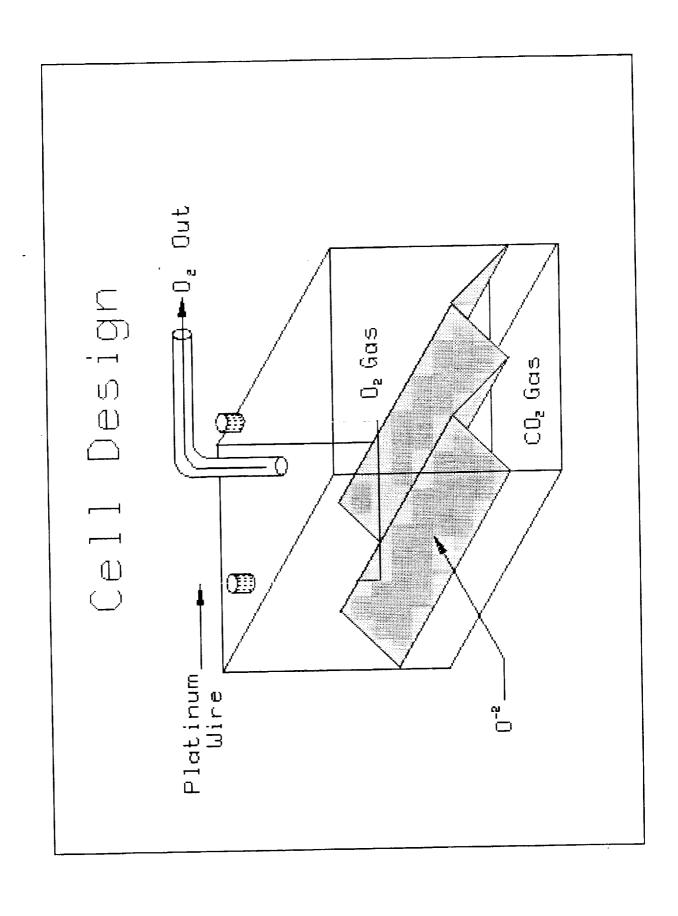
Sample # 1 Sample # 2

Percent Finer Than



Appendix C

Cell Design



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